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Crystalline Tungsten Sulfide Thin Films by Atomic Layer Deposition and Mild Annealing

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Tungsten disulfide (WS₂) is a semiconducting 2D material, which is gaining increasing attention in the wake of graphene and MoS₂ owing to its exciting properties and promising performance in a multitude of applications. Herein, we deposited WS_x thin films by atomic layer deposition (ALD) using W₂(NMe₂)₆ and H₂S as precursors. The films deposited at 150 °C were amorphous and sulfur deficient. The amorphous films crystallized as WS₂ by mild post-deposition annealing in H₂S/N₂ atmosphere at 400 °C. Detailed structural characterization using Raman spectroscopy, X-ray diffraction, and transmission electron microscopy revealed that the annealed films consisted of small (<10 nm) disordered grains. Our approach enables deposition of continuous and smooth WS₂ films down to a thickness of a few monolayers while retaining a low thermal budget compatible with potential applications in electronics as well as energy production and storage, for example.

I. INTRODUCTION

The remarkable demonstration of producing graphene, a stable, one-atom-thick layer of carbon by simply exfoliating a bulk crystal with adhesive tape in 2004¹ led to a rapid increase in studies of a variety of two-dimensional (2D) materials and their evaluation for applications including electronics, optoelectronics, catalysis, and energy storage.^{2–7} The huge interest in 2D materials stems from their unique properties that originate from their layered crystal structures as well as from their stability in ultrathin form of a few to only one atom(s) thick.^{8,9} In particular, during the last few years intense attention has been given to the broad and versatile group of transition metal dichalcogenides (TMDCs), which includes metals and semimetals as well as semiconductors with band gaps varying from less than 1 to nearly 3 eV.^{2,3,10,11} The properties of TMDCs can be further tailored by controlling their thickness,^{12,13} surface functionalization,¹⁴ strain,^{15,16} doping and alloying,^{17,18} and creating heterostructures with other 2D materials.^{8,17,19}

Tungsten disulfide (WS₂) is a semiconducting TMDC, which has an indirect band gap of 1.3–1.4 eV in bulk in the common 2H and 3R phases, which have trigonal prismatic coordination around tungsten and only differ in the stacking of the WS₂ layers.^{3,20} The band gap of WS₂ increases with decreasing thickness and, intriguingly, becomes direct at monolayer thickness with a magnitude of approximately 2.0 eV for the optical band gap.^{13,21} The electronic structures of 2H and 3R WS₂ make them suitable for many semiconductor applications such as field-effect transistors,^{22,23} photodetectors,^{6,24} and photocatalysis,^{25,26} while other promising applications, such as electrocatalysis²⁷ and supercapacitors²⁸ benefit from the increased electrical conductivity of the metastable, metallic 1T-phase of WS₂, which has octahedral coordination around tungsten.

For many of the aforementioned applications, WS₂ should be deposited as continuous films of accurately controlled thickness on large or nanostructured substrates, preferably at low

temperatures. Gas phase methods such as chemical vapor deposition (CVD) and atomic layer deposition (ALD) hold the greatest promise in meeting these requirements. Excluding the top-down exfoliation methods of bulk crystals, CVD is currently the main method used to deposit high-quality crystals and films of WS_2 and other TMDCs.^{3,29} However, these CVD processes require high deposition temperatures of 550–750, 700–1000 or 700–1100 °C when using $\text{W}(\text{CO})_6$,^{23,30} WCl_6 ,^{31,32} or the poorly volatile WO_3 ^{33–35} as the tungsten precursor, respectively. Furthermore, large-area continuous WS_2 films are rarely achieved using these processes. Another bottom-up approach to produce WS_2 is sulfurization of W or WO_3 films deposited by evaporation, sputtering, or ALD, for example. Although sulfurization can produce uniform, continuous films on large substrates, the films typically have limited grain size ranging from a few to a few tens of nm despite the use of high temperatures, typically 750–1000 °C.^{3,36,37}

ALD, which is often considered to be an advanced variant of CVD, is a gas-phase thin film deposition technique that is based on self-limiting surface reactions.^{38–40} Contrary to CVD, gas phase reactions and self-decomposition of precursors are avoided in ALD by pulsing the precursors alternately (separated by purge steps) and by using deposition temperatures below the decomposition temperatures of the precursors, respectively. Advantages of ALD include excellent reproducibility and facile thickness control achieved by changing the number of ALD cycles as well as extreme thickness uniformity and conformality. ALD films are usually of high quality despite the use of relatively low deposition temperatures, often 100 to 400 °C. Furthermore, ALD is also easily scalable for industrial use.^{40,41}

In recent years, ALD has been increasingly studied for the deposition of various TMDCs, although so far most studies have focused on MoS_2 .⁴² On the contrary, only a few processes have been demonstrated for WS_2 . WF_6 does not enable film growth with H_2S unless a H_2

plasma pulse^{43–46} is added before the H₂S pulse or either a ZnS substrate or a ZnEt₂ pulse^{47–49} is applied. W(CO)₆ can be used to deposit amorphous or nanocrystalline WS₂ films with either H₂S^{50,51} or H₂S plasma⁵² reactants. The use of WCl₅ with H₂S has also been claimed, but very limited information is available about the precursor as well as the process and its ALD characteristics.⁵³ Furthermore, in many cases the ALD WS₂ films have been tens to hundreds of nm in thickness – indeed, in addition to the WCl₅+H₂S process, ultrathin (<10 nm) films have only been deposited by the W(CO)₆+H₂S plasma⁵² and WF₆+H₂ plasma+H₂S^{43–46} PEALD processes operated at 350 and 250–450 °C, respectively. Herein, we report a low-temperature ALD process for the deposition of tungsten sulfide thin films. Using W₂(NMe₂)₆ and H₂S as the precursors, amorphous films are deposited at 150 °C. A 400 °C post-deposition annealing step in H₂S/N₂ atmosphere is added to crystallize the films as semiconducting WS₂. We show that the process can be used to produce crystalline ultrathin (<10 nm) WS₂ films while maintaining a low thermal budget.

II. EXPERIMENTAL

Tungsten sulfide thin films were deposited in a commercial, hot wall, cross-flow F120 ALD reactor⁵⁴ operated at approximately 5 mbar. Nitrogen (N₂, AGA, 99.999%) served as both the carrier and the purge gas. The substrates were soda lime glass and silicon (100) with size up to 5 × 5 cm², the latter covered by either a native oxide or a 90 nm thermal SiO₂ layer. The glass substrates were cleaned using successive ultrasonic baths of alkaline ultrasonic cleaning solution, tap water, ethanol, and de-ionized water. The silicon substrates were blown clean of particles using pressurized nitrogen. The native silicon oxide layer was not removed.

The dimeric tungsten(III) amide W₂(NMe₂)₆ was synthesized following a published procedure⁵⁵ with slight modifications (yield 69.5%). W₂(NMe₂)₆ was heated to 120 °C in an open glass boat inside the ALD reactor and pulsed by inert gas valving. H₂S (AGA, 99.5%) was fed into the reactor at a flow rate of approximately 14 sccm through a mass flow meter and a needle valve. H₂S was pulsed using solenoid valves. For most experiments, excluding the initial depositions of thicker films using 500 cycles, N₂ and H₂S were further purified using SAES Microtorr MC1-902F and MC1-302F gas purifiers, respectively.

Post-deposition annealing treatments were done for selected films inside the F120 ALD reactor under a flowing atmosphere of N₂ (400 sccm, approximately 5 mbar) mixed with H₂S (14 sccm) for 1 h at 300 to 500 °C. Both gases were fed through gas purifiers as described above.

Thermogravimetric analysis (TGA) of W₂(NMe₂)₆ was performed under atmospheric pressure of N₂ using a Mettler Toledo STARe system equipped with a

TGA850 thermobalance. The heating rate was 10 °C/min and the sample size was approximately 10 mg.

Film thicknesses were measured by energy-dispersive X-ray spectroscopy (EDS, Oxford INCA connected to a Hitachi S-4800 SEM) and X-ray reflectivity (XRR, Rigaku Smartlab or PANalytical X'Pert Pro). EDS thicknesses were calculated from W L α and S K α X-ray lines using the GMRFilm software,⁵⁶ assuming WS₂ bulk density of 7.6 g/cm³.⁵⁷ EDS and XRR also provided information on the S/W atomic ratio and the film density, respectively.

Film morphology and roughness were studied by atomic force microscopy (AFM, Veeco Multimode V). AFM imaging was performed in ambient air in tapping mode using silicon probes with a tip radius of less than 10 nm (Bruker). The images were flattened to remove artefacts caused by sample tilt and scanner nonlinearity. Film roughness was calculated as a root mean square value (R_q) from $2 \times 2 \mu\text{m}^2$ images.

Film crystallinity was examined by X-ray diffraction (XRD, Rigaku Smartlab) using Cu K α ($\lambda = 1.54 \text{ \AA}$) X-ray beam in grazing incidence (incident angle of 1°) geometry as well as by Raman spectroscopy in backscattering geometry using a confocal Raman microscope (NT-MDT Ntegra) with a 100 \times objective and a 532 nm laser.

The composition of the surface layers was analyzed by X-ray photoelectron spectroscopy (XPS), using an Argus Spectrometer (Omicron NanoTechnology GmbH) operating at a pass energy of 20 eV. Samples were illuminated with X-rays emitted from a standard Mg source (K α line) at a photon energy of 1253.6 eV. No sputtering was performed on the samples. Binding energies were calibrated using the C 1s peak (284.8 eV) of ambient hydrocarbons, and peak fitting was done using the CasaXPS software.

Film composition averaged over the film thickness was analyzed by time-of-flight elastic recoil detection analysis (ToF-ERDA) using a 50 MeV $^{79}\text{Br}^{7+}$ ion beam. The incident and scattering angles were 16 and 40 degrees, respectively.

Cross-sectional high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging was performed using a Hitachi HD2700 aberration corrected microscope at EAG Laboratories. The TEM sample was prepared by lift-out method using a focused ion beam instrument.

III. RESULTS AND DISCUSSION

A. Film deposition and characterization of as-deposited films

We deposited tungsten sulfide thin films by ALD using a dimeric tungsten amide complex hexakis(dimethylamido)ditungsten(III) [$\text{W}_2(\text{NMe}_2)_6$] and hydrogen sulfide (H_2S) as precursors. TGA of $\text{W}_2(\text{NMe}_2)_6$ confirmed its volatility, but the residual mass of 11.8%, although much below the theoretical tungsten content of 58.2 mass-%, suggests that thermal decomposition started to occur below 300 °C (Fig. 1). $\text{W}_2(\text{NMe}_2)_6$ was heated to 120 °C for the film deposition experiments. Saturation of the growth rate, as is characteristic to ALD, was reached at 150 °C using $\text{W}_2(\text{NMe}_2)_6$ and H_2S pulses of at least 0.5 and 2.0 s, respectively (Fig. 2a,b). The growth rate determined by EDS was approximately 0.7 Å/cycle, whereas XRR indicated a slightly higher growth rate of approximately 0.8 Å/cycle. This difference is likely caused by the use of bulk density as well omission of impurities in the EDS thickness calculations. According to XRR, the actual film density was 7.0–7.2 g/cm³, slightly below the WS_2 bulk density of 7.6 g/cm³.⁵⁷

EDS revealed that the films were sulfur deficient compared to the target WS_2 stoichiometry as well as the W_2S_3 stoichiometry expected from the +3 oxidation state of tungsten in the precursor, although using longer H_2S pulses clearly increased the S/W atomic ratio. The film thickness increased linearly with increasing number of ALD cycles showing little to no nucleation delay (Fig. 2c).

The deposition temperature had a strong effect on both the growth rate and the film composition. The growth rate increased and the S/W ratio decreased with increasing temperature (Fig. 2d). The lowest deposition temperature of 130 °C was limited by the

source temperature of the tungsten precursor (120 °C), whereas the highest deposition temperature was set by decomposition of the tungsten precursor, which was observed to start at 200 °C as seen by coloration of the glass source tube of the ALD reactor. Interestingly, although the self-limiting ALD behavior was lost at 200 °C, the films deposited at 200 to 300 °C were relatively uniform, metallic by appearance, and conductive with resistivities of 800–1000 $\mu\Omega\text{cm}$. This suggests that $\text{W}_2(\text{NMe}_2)_6$ may also be a useful low-temperature CVD precursor for tungsten.

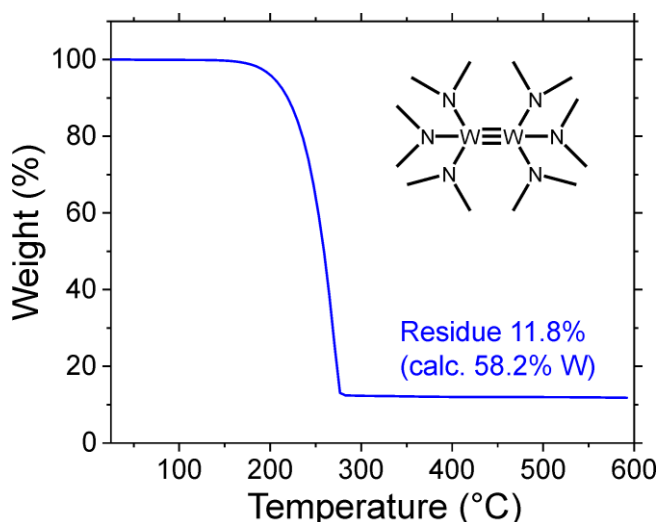


FIG. 1. TGA of $\text{W}_2(\text{NMe}_2)_6$ (structure shown as an inset) under a N_2 atmosphere.

The as-deposited films were practically amorphous, although an unidentified X-ray reflection at approximately $9^\circ 2\theta$ was detected in the thickest films deposited using 500 cycles (Fig. S1 in supplementary material).⁵⁸ The peak position corresponds to a d-spacing of approximately 10 Å, which is to be compared with the 6.1–6.2 Å spacing of the (002) planes in 2H or 3R WS_2 (Powder Diffraction files PDF 8-0237 and 35-0651, respectively). Such interlayer expansion has been demonstrated for layered TMDCs including MoS_2 and WS_2 by intercalating various ions, molecules, or graphene sheets, for

example.⁵⁹ Here, the expansion may be due to impurities or disordered WS_x species inside the van der Waals gap of WS₂. Weak peaks attributed to WS₂ were also detected by Raman spectroscopy, although the laser seemed to crystallize WS₂ during the measurements, despite the use of a very low laser power (Fig. S2 in supplementary material).⁵⁸ Thus, the as-deposited films appear to be poorly ordered structurally, although some hints of WS₂ formation were observed.

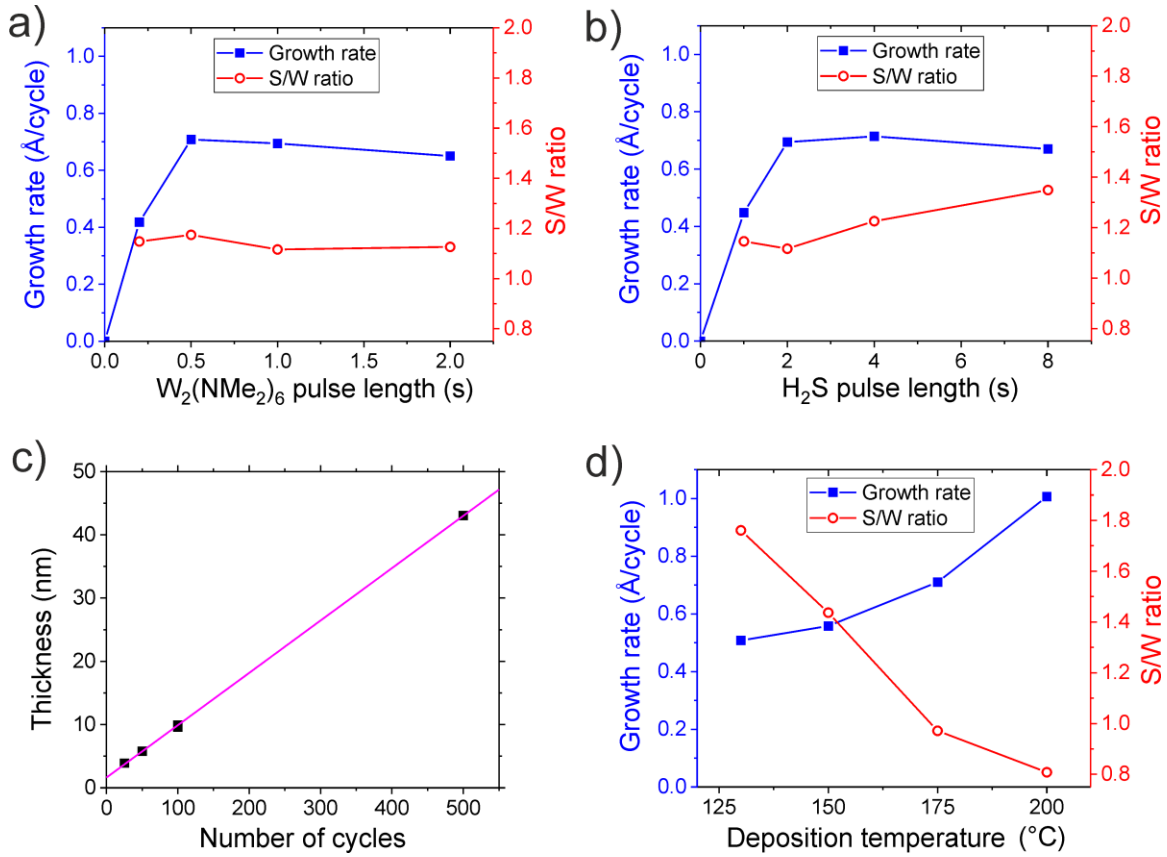


FIG. 2. Growth rate and S/W ratio versus a) $W_2(NMe_2)_6$ and b) H_2S pulse length. c) Film thickness versus number of ALD cycles. d) Growth rate and S/W ratio versus deposition temperature. Film thicknesses were measured by EDS (a,b,d) or XRR (c). S/W ratio was measured by EDS. Unless otherwise noted, the films were deposited on native oxide covered silicon substrates at 150 °C using 500 cycles with 1 s $W_2(NMe_2)_6$ and 2 (a) or 4 s (c,d) H_2S pulses separated by 3 (a,b) or 2 s (c,d) N_2 purges. The line in c) represents a linear fit to the data, whereas the other lines are only to guide the eye.

The films were very smooth: a 500 cycle film deposited at 150 °C, for example, had a root-mean-square roughness (R_q) of only 0.4 nm (Fig. S3 in supplementary material).⁵⁸ The tungsten sulfide films had a metallic, reflective appearance, which was supported by optical transmittance measurements showing low transmittance from UV to 1100 nm and no evidence of a band gap (Fig. S4 in supplementary material).⁵⁸ The resistivity of the films ranged from 1 to 10 m Ω cm, further corroborating the metallic conductivity of the as-deposited films. The reason for the metallic behavior is not known at present, but is not completely unexpected, as the 1T phase of WS₂ is metallic. Impurities or sulfur vacancies, for example, could also explain the metallic behavior via heavy doping or the formation of metallic WN_x or WC_x species, for example.

Table I. Elemental composition of an as-deposited tungsten sulfide film averaged over the 40 nm film thickness and on the surface as measured by ToF-ERDA and XPS, respectively. The film was deposited on silicon at 150 °C using 500 cycles.

Element	Average (at-%)	Surface (at-%)
	ToF-ERDA	XPS
W	37.9±0.2	24.7
S	42.0±0.7	21.8
S/W	1.11±0.02	0.88
C	7.1±0.4	29.5
N	3.3±0.3	1.9
O	3.8±0.3	22.1
H	5.8±1.2	Not detectable

The average and surface compositions of an approximately 40 nm film were analyzed by ToF-ERDA and XPS, respectively (Table I). The film was sulfur-deficient and contained carbon, nitrogen, oxygen, and hydrogen impurities. The average S/W ratio of 1.11 is in agreement with the EDS results presented earlier and much lower than that expected for either W_2S_3 (1.5) or WS_2 (2.0). The high surface carbon content detected by XPS is due to atmospheric contamination, as the films were not sputtered prior to the analysis. Oxygen appears to originate from surface oxidation of the films in air, whereas the other impurities detected by ToF-ERDA (C, N, H) are likely due to incomplete removal of the ligands of the $W_2(NMe_2)_6$ precursor. The impurity contents were similar to those of the ALD tungsten oxide and nitride films deposited using the same tungsten precursor, except for the lower hydrogen content of our WS_x films.^{60,61}

B. Post-deposition annealing

In order to crystallize the films, we annealed them in the ALD reactor in a flowing H_2S/N_2 (14/400 sccm, ~5 mbar total pressure) atmosphere. This approach has proven to be effective in producing crystalline and smooth SnS_2 films while retaining a low thermal budget and requiring no additional annealing equipment.⁶² Initially, temperatures from 300 to 500 °C were tested for approximately 9 nm thick tungsten sulfide films deposited using 100 cycles.

While annealing at 300 °C resulted in little improvement in the crystallinity of the films, annealing at 400 and especially 500 °C led to a clear increase in the intensities of the Raman (Fig. 3a) and XRD (Fig. 3b) peaks attributed to the 2H or 3R phase of WS_2 . Both the 2H and 3R phases have similar structures differing only by the stacking of the WS_2 layers.³ Thus, we could not distinguish between them or other stacking

arrangements. The broadness of both the Raman and the XRD peaks even after annealing suggests that the films were nanocrystalline. The surface composition also improved with the best results seen after the annealing at 400 °C, resulting in a S/W ratio of 1.82 (Table II). The slight sulfur deficiency may be due to surface oxidation, which is commonly observed for synthetic WS₂ and other TMDCs.^{63–65} Increasing the annealing temperature to 500 °C resulted in a lower S/W ratio and a higher oxygen content compared to the films annealed at 400 °C, perhaps due to the rough morphology discussed below. The nitrogen content decreased to one third of the original (as-deposited) value after annealing at 400 °C, which suggests removal of impurities from the films during annealing. Unfortunately, we were unable to reliably determine the carbon and hydrogen contents of the films after annealing, as the annealed films were too thin for ToF-ERDA and the ambient hydrocarbon contamination distorted the carbon levels detected by XPS.

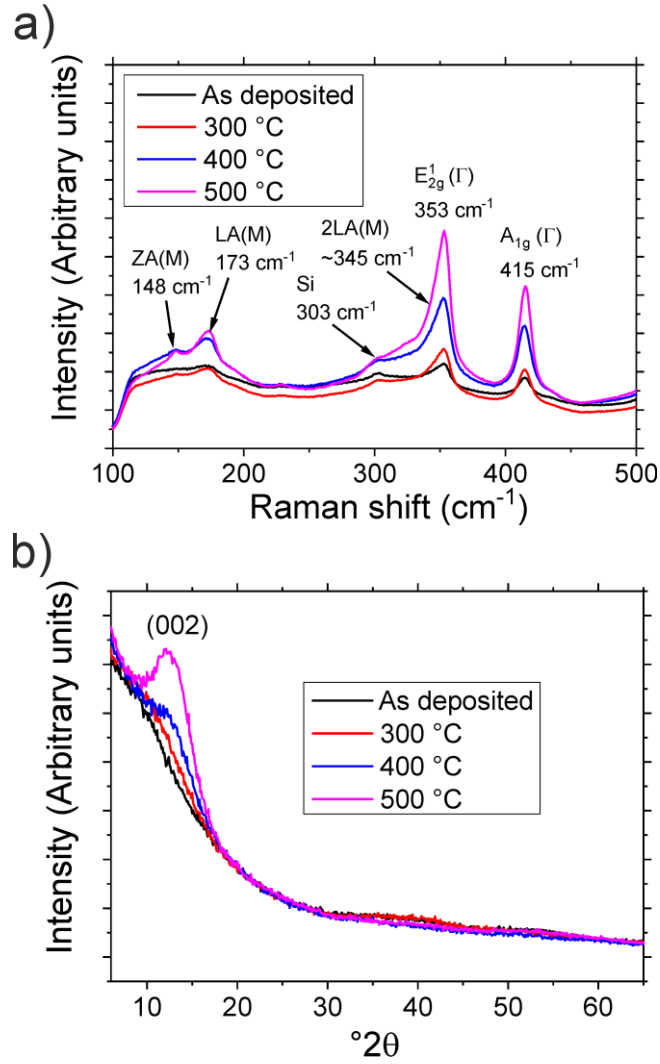


FIG. 3. a) Raman spectra and b) grazing incidence X-ray diffractograms of tungsten sulfide films as-deposited and after annealing at different temperatures. The films were deposited on silicon at 150 °C using 100 cycles and the annealing was done in $\text{H}_2\text{S}/\text{N}_2$ atmosphere for 1 h. The Raman and XRD peaks of WS_2 were indexed according to Ref.66 and Powder Diffraction File (PDF) 8-0237, respectively.

Table II. Elemental surface composition of tungsten sulfide films as-deposited and after annealing as analyzed by XPS. The films were deposited on silicon at 150 °C using 100 cycles and the annealing was done in $\text{H}_2\text{S}/\text{N}_2$ atmosphere for 1 h.

Element	As-deposited	300 °C	400 °C	500 °C
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	(at-%)	(at-%)	(at-%)	(at-%)
W	22.6	21.4	16.2	17.1
S	19.6	26.0	29.5	26.7
S/W	0.87	1.22	1.82	1.56
C	30.2	33.8	37.9	27.9
N	3.1	1.8	1.0	0.8
O	24.6	16.9	14.2	27.5

Core-level photoelectron spectra of W 4f and S 2p regions corroborated 400 °C as the optimal annealing temperature. Three doublets were fitted to the W 4f spectra representing WS₂ at binding energies of 32.4 and 34.6 eV for the W 4f_{7/2} and W 4f_{5/2} levels, respectively, WS_xO_y or WO₂ at binding energies of 33.3 and 35.5 eV, and WO₃ at 35.8 and 38.0 eV (Fig. 4a).^{67–69} The binding energies of the WS₂ doublet are in agreement with the semiconducting 2H or 3R phases of WS₂, whereas the metallic 1T phase would result in lower binding energies.^{3,67–69} The WO₃ content relative to the total W content, which likely originates from the oxidation of the films in air, was the lowest at 17% in the sample annealed at 400 °C, compared with 51% in the as-deposited film and 32 and 23% in the films annealed at 300 and 500 °C, respectively. Similarly, the relative WS₂ content reached its maximum (74%) after annealing at 400 °C.

The S 2p region expectedly contained a doublet corresponding to S²⁻ in WS₂ with binding energies of 162.1 (S 2p_{3/2}) and 163.3 eV (S 2p_{1/2}) as shown in Figure 4b.^{67–70} The broadening of the S 2p peak was attributed to the presence of substoichiometric WS_z (z < 2) at binding energies of 161.2 and 162.4 eV and sulfur in oxysulfide or organic environment at 163.3 and 164.4 eV for the S 2p_{3/2} and S 2p_{1/2} levels, respectively.^{68–70}

The relative content of the WS₂-bound sulfur to the total sulfur content increased with increasing annealing temperature from 47% in the as-deposited film to 68, 71, and 78 % in the films annealed at 300, 400, and 500 °C, respectively. The improvement was also qualitatively seen in the improved resolution of the S 2p doublet with increasing annealing temperature.

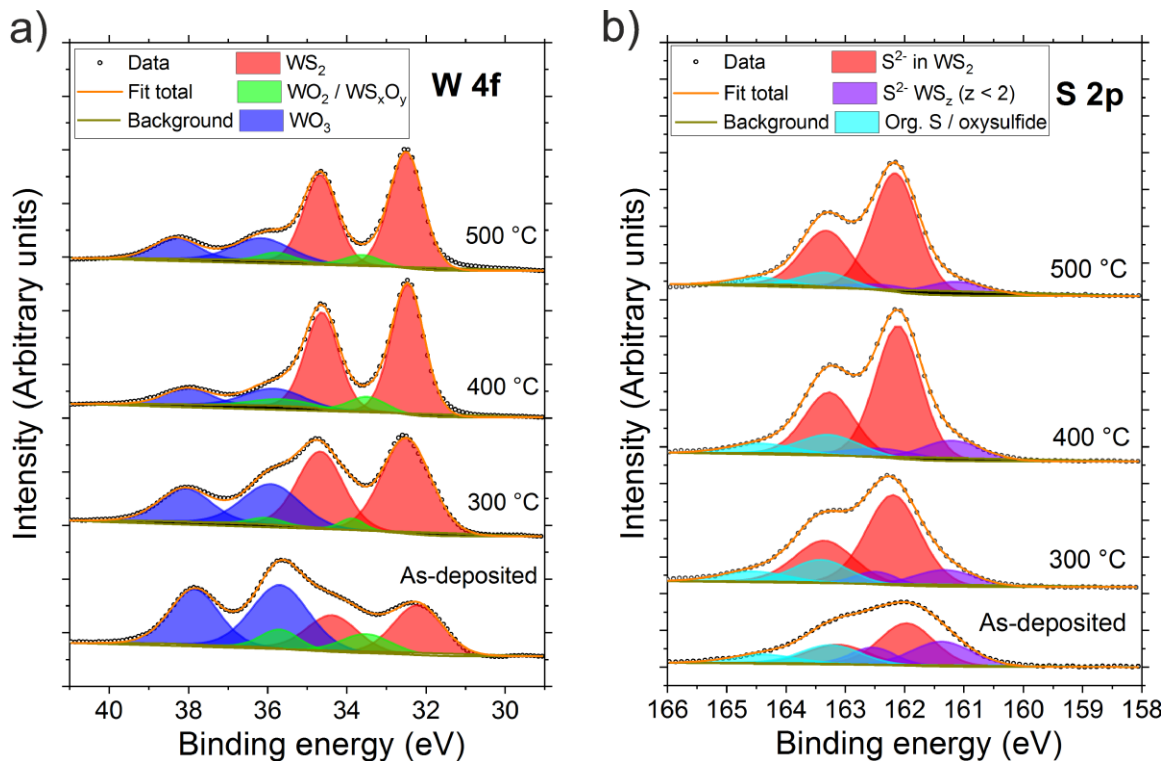


FIG. 4. X-ray photoelectron spectra of a) W 4f and b) S 2p regions. The films were deposited on silicon at 150 °C using 100 cycles. The annealing was done in H₂S/N₂ atmosphere for 1 h.

The films remained smooth when annealed at 400 °C or below, whereas annealing at 500 °C led to a very rough morphology with up to 50 nm high particles or crystallites present on the surface of the nominally 9 nm thick film (Fig. 5).

Further evidence for the formation of WS₂ at 400 °C and above was obtained from optical transmission measurements, which showed a clear change compared to the

as-deposited films (Fig. S5 in supplementary material).⁵⁸ Using a Tauc plot, an indirect band gap of approximately 1.2 eV, close to the WS₂ bulk band gap of 1.3–1.4 eV,²⁰ was estimated for the films annealed at 400 and 500 °C. Notably, this is in contrast to the apparently metallic behavior of the as-deposited films.

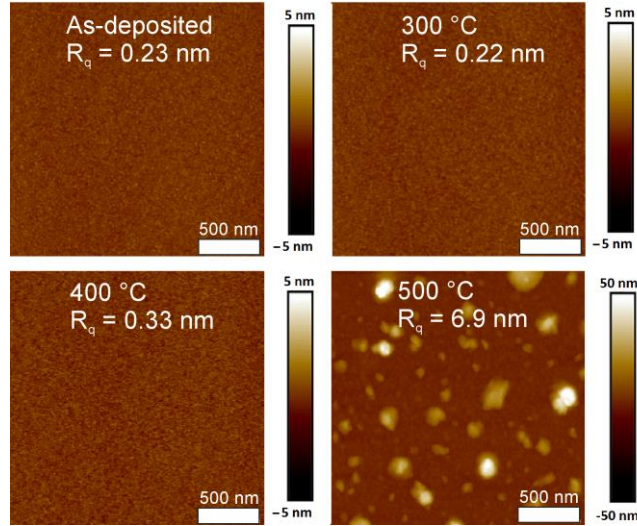


FIG. 5. AFM images and roughness (R_q) values of tungsten sulfide films as-deposited and after annealing at different temperatures. Note the different height scale for the sample annealed at 500 °C. The films were deposited on silicon at 150 °C using 100 cycles and the annealing was done in H₂S/N₂ atmosphere for 1 h.

C. *Scaling down the thickness: towards few-layer WS₂*

We proceeded to produce ultrathin (<10 nm) WS₂ films by annealing the as-deposited films at 400 °C, the temperature which offered the best combination of crystallinity, stoichiometry, and smooth morphology. Linear thickness control was demonstrated to hold also at thicknesses below 10 nm (Fig. 6a). Although we were unable to determine the thickness of the thinnest film deposited using 10 cycles, linear fit suggests its thickness to be close to 1.2 nm, which corresponds to two monolayers of WS₂ (monolayer thickness 0.62 nm). Furthermore, all of the the films deposited using 10

to 100 cycles were very smooth and continuous even after the 400 °C post-deposition annealing treatment (Fig. 6b).

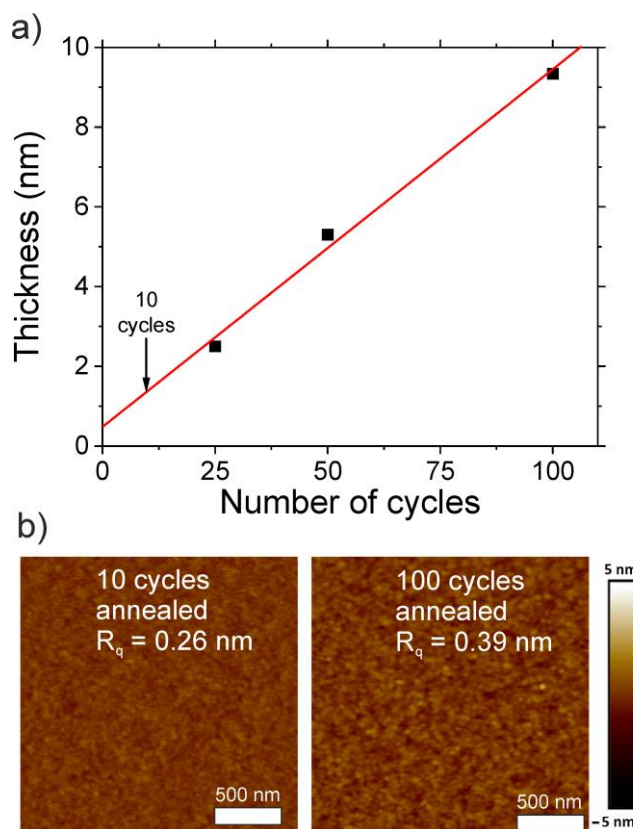


FIG. 6. a) Thickness of annealed tungsten sulfide films, where the red line represents linear fit to the data and arrow shows the estimated thickness of the 10 cycle film assuming linear growth. b) AFM images of annealed tungsten sulfide films. The films were deposited at 150 °C and annealed at 400 °C for 1 h.

Raman spectroscopy confirmed that the 10 to 100 cycle films crystallized as WS₂ when annealed at 400 °C (Fig. 7a). For simplicity, the Raman modes discussed here are denoted according to the D_{6h} symmetry of bulk 2H-WS₂. As reported for 2H-WS₂, in addition to the E_{12g} and A_{1g} modes at the center of the Brillouin zone, longitudinal acoustic mode at the M point of the Brillouin zone LA(M) and its overtone 2LA(M) were observed due to resonance effects with the 532 nm laser.⁶⁶ To properly fit the low-

frequency side of the $E_{2g}^1/2LA(M)$ peak, a broad mode near 330 cm^{-1} was also included. This mode was denoted as the $E_{2g}^1(M)$ mode according to Su et al.,⁷¹ although Liu et al.⁷² suggested this to be the $B_{2g}^1(K)$ and Zhang et al.⁷³ the $E''(M)^{TO}$ mode (Fig. 7b).

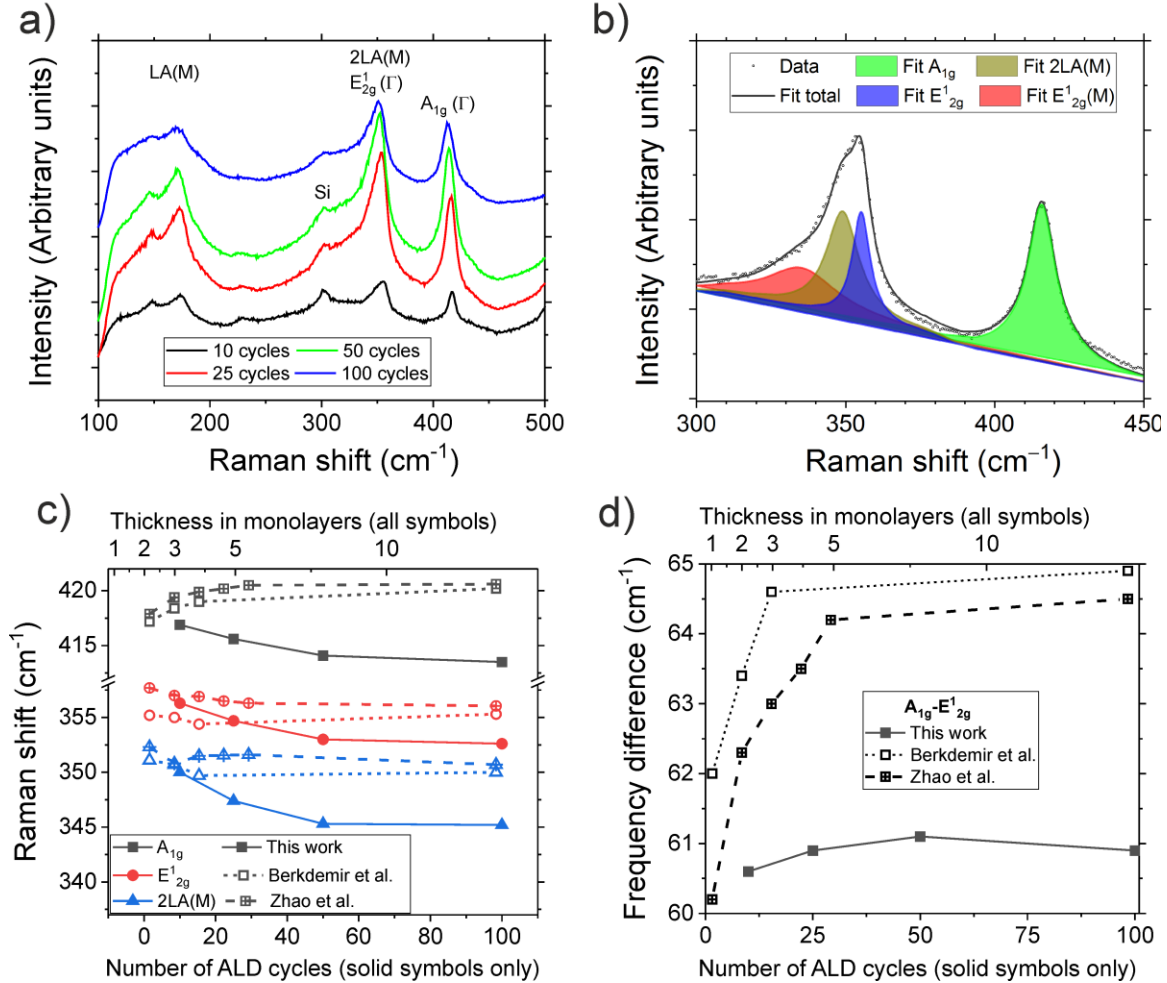


FIG. 7. a) Raman spectra of WS_2 films of different thicknesses after annealing at $400\text{ }^\circ\text{C}$. b) Raman spectrum of a 25 cycle WS_2 film annealed at $400\text{ }^\circ\text{C}$ showing the modes fitted between 300 and 450 cm^{-1} . c) Fitted positions of the A_{1g} , E_{2g}^1 , and $2LA(M)$ modes and d) frequency difference $A_{1g}-E_{2g}^1$ of WS_2 films of different thicknesses. Open and crossed symbols in c) and d) represent literature values from Berkdemir et al. (CVD-grown flakes)⁶⁶ and Zhao et al. (exfoliated flakes),⁷⁴ respectively.

Frequencies of the Raman modes are commonly used to determine the thickness of WS₂ and other TMDCs, especially at thicknesses below 5 monolayers.^{66,74,75} Typically, a blueshift of the in-plane E_{2g}¹ (increase of Raman shift/frequency) and a redshift of the out-of-plane A_{1g} mode (decrease of Raman frequency) are observed with decreasing thickness, which results in decreased separation between these two modes.^{66,74,75} Here, however, the A_{1g}, E_{2g}¹, and 2LA(M) modes were all observed to blueshift when the number of ALD cycles (thickness) was decreased (Fig. 7c), whereas the A_{1g}–E_{2g}¹ frequency difference changed by no more than 0.5 cm⁻¹ (Fig. 7d). Thus, the mode frequencies observed for exfoliated WS₂ flakes, as studied by Zhang et al.,⁷³ or CVD-grown triangular flakes, as studied by Berkdemir et al.,⁶⁶ cannot be used to determine the thicknesses of our films.

Two possible explanations for the different frequency-thickness trends observed here are the strain and doping of the films, both of which are known to affect the Raman frequencies of TMDCs.^{15,16,18,71,75} Strain is often formed in TMDCs as a result of different thermal expansion of the film and the substrate as well as film-substrate bonding. Here, the changes in film composition and structure during annealing are also likely to affect the strain. The positions of the in-plane E_{2g}¹ mode and the 2LA(M) mode are sensitive to in-plane strain, showing redshifts of 2–3 cm⁻¹ per one percent of tensile strain,¹⁵ whereas the out-of-plane A_{1g} mode is expected to be sensitive to out-of-plane strain. Studies of WS₂ monolayers on different substrates have also shown changes in frequencies of up to 5 cm⁻¹ for both the A_{1g} and the E_{2g}¹ modes depending on the substrate, at least partly due to strain.^{71,76} The observed redshifts especially in our thicker films would imply a tensile strain. Regarding doping, a redshift of the A_{1g}, and to a

smaller degree of the E_{2g}^1 mode, has been observed with increasing carrier concentration.^{18,77} We speculate that strain may be the most likely explanation for the observed Raman shifts in our films due to the relatively large magnitude of the observed redshifts, the increase of the redshifts with increasing thickness as well as the disordered film structure, which will be discussed later.

The Raman peaks of our WS_2 films were relatively wide: the full-width at half-maximum (FWHM) values of the A_{1g} and E_{2g}^1 peaks increased from about 8 and 6 to 9 and 14 cm^{-1} , respectively, when the number of ALD cycles was increased from 10 to 100 (Fig. S6 in supplementary material).⁵⁸ WS_2 flakes exfoliated from bulk crystals have been reported to have FWHM of 2–4 cm^{-1} for these modes,^{44,74} which suggests that our films exhibit considerable disorder compared to pristine WS_2 . Additionally, the disorder seems to increase with increasing number of ALD cycles, consistent with the mode frequencies shifting further away from their expected values. For comparison, a 3 ML thick PEALD WS_2 film grown at 300 °C had FWHM of 9 and 5 cm^{-1} for the A_{1g} and E_{2g}^1 modes, respectively.⁴⁴ On the other hand, 4 ML WS_2 films produced by sulfurizing ALD- WO_3 films yielded A_{1g} and E_{2g}^1 FWHM as large as 16 and 10 cm^{-1} when the sulfurization was done at 600 °C, and still 12 and 9 cm^{-1} for the films sulfurized at 900 °C.⁷⁸

The microstructure of an annealed 50 cycle WS_2 film was further evaluated by HAADF-STEM. The film was observed to be smooth and continuous, in accordance with the AFM results (Fig. 8a). The film thickness of approximately 5.5 nm, corresponding to about 9 monolayers of WS_2 , was in excellent agreement with XRR (5.3 nm). Furthermore, the film had a sharp interface with the native oxide layer underneath and no obvious oxidized layer was observed on top of the film. The WS_2 film consisted of small,

about 3–10 nm wide crystallites, which exhibited the expected layered structure of WS₂ (Fig. 8). However, the basal planes were found to be randomly oriented with respect to the substrate and even strongly bent in several locations. Additionally, many of the crystallites appeared to be only a few monolayers thick (Fig. 8c). This disordered structure is in accordance with the observed wide XRD and Raman peaks and may explain the different Raman shifts compared to exfoliated and CVD-grown flakes. According to the HAADF-STEM images, the distance between the (002) basal planes varied between approximately 6 and 7 Å with an average of 6.5 Å, which is slightly more than the expected values of 6.18 Å or 6.13 Å for the 2H and 3R phases (PDF 8-0237 and 35-0651, respectively). Another set of planes was observed with an interplane spacing of 2.8 Å, which is in good agreement with the (100) and (101) planes of WS₂ with expected spacings of approximately 2.7 Å. Unfortunately, we could not definitively identify whether the layers were stacked in 2H, 3R, or some other polytype.

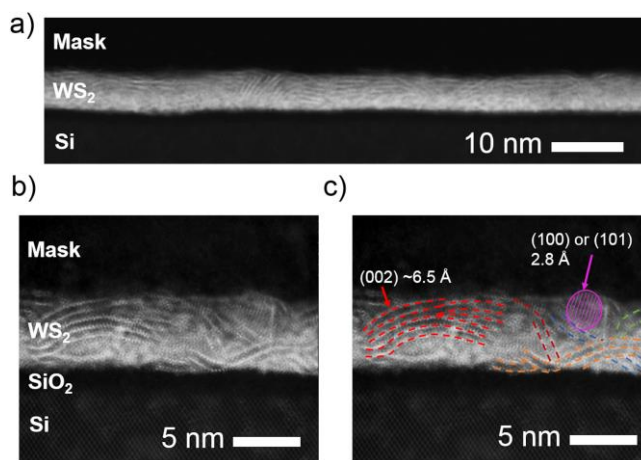


FIG. 8. a) Low and b) high magnification HAADF-STEM images of a 50 cycle WS₂ film annealed at 400 °C. c) (002) (dashed) and (100) or (101) planes (solid) highlighted in the high magnification image along with the estimated interplane distances.

D. Comparison to other processes

Finally, we briefly compare our process and the deposited films to the existing WS₂ ALD processes (Table III). Our deposition temperature of 150 °C is the lowest among the reported processes, and even our annealing temperature of 400 °C is similar to the deposition temperature of many of the WS₂ ALD processes. Therefore, it is not surprising that the deposited films were amorphous similar to the W(CO)₆+H₂S process operated at 165–205 °C. Unfortunately, the comparison to our well-behaving ALD process is hindered by the fact that the saturative nature of the surface reactions, an important characteristic of ALD, has not been evaluated for many of the reported processes. Furthermore, prior to our work, only a few of the reported processes have been used to deposit ultrathin 2D films of WS₂. The composition and structure of our annealed films as judged by the S/W ratio as well as the grain size are similar to most of the processes. So far, the best crystallinity seems to have been obtained using plasma-enhanced ALD, but the use of plasma adds process complexity and may limit the conformality of the films. Detailed studies on issues critical to the growth of 2D films, including nucleation, grain growth, film closure, and effect of substrate have been performed with the WF₆+H₂ plasma+H₂S process,^{43–46} whereas corresponding understanding is lacking for the other reported processes. Thus, further studies on our process as well as the other processes are needed in the future to assess their full potential in the growth of 2D WS₂.

Table III. Reported WS₂ ALD processes and characteristics of deposited films.

Precursors	Deposition (annealing) temperature (°)	Growth rate (Å/cycle)	Satura tion	Thickness (nm)	Grain size (nm)	S/W ratio	Ref.
W ₂ (NMe ₂) ₆ + H ₂ S	150 (400)	0.8–0.9	yes	~2–10	~3–10	1.8	This work
WF ₆ + H ₂ S ^b	300–350	~1	- ^a	10–300	5–100	-	47,49
WF ₆ + H ₂ plasma + H ₂ S	250–450	~0.2	yes	~1–3	~10	1.8±0. 1	43–45
	450	~0.2	yes	<1–5	up to 200	1.8±0. 1	46
WCl ₅ + H ₂ S	390	1.25	- ^a	<5	cryst. ^c	-	53
W(CO) ₆ + H ₂ S	165–205	~0.2	yes	20–40	amorph	2.05	50
	400	3.6	- ^a	175	~5	-	51
W(CO) ₆ + H ₂ S plasma	350	~1	yes	3–20	3–7	1.94	52

^aNot evaluated, ^bno growth unless ZnS substrate or ZnEt₂ pulses were applied, ^cfilm crystalline, but grain size not indicated.

IV. SUMMARY AND CONCLUSIONS

In this work, we demonstrated atomic layer deposition of tungsten sulfide thin films using a dimeric amide $W_2(NMe_2)_6$ and H_2S as precursors. The process exhibited good ALD characteristics at a low temperature of 150 °C. The as-deposited films were smooth and amorphous with a S/W atomic ratio close to 1 and apparently metallic behavior. A post-deposition annealing treatment in H_2S/N_2 atmosphere at 400 °C, a low temperature compared to most previous studies on WS_2 , resulted in near-stoichiometric, crystalline, and semiconducting WS_2 films. We demonstrated that crystalline and smooth WS_2 films can be deposited in a wide thickness range from a few monolayers to ten nm using the present process. Detailed inspection of film microstructure using Raman spectroscopy, XRD, and HAADF-STEM showed that the films were composed of randomly oriented, nanocrystalline WS_2 grains exhibiting notable disorder. Supported by the excellent scalability and thickness control of ALD as well as the relatively low thermal budget, our process might be especially interesting for large-scale energy applications including lithium-ion batteries and hydrogen evolution reaction, where a defect-rich structure is often beneficial.

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Table I. Elemental composition of an as-deposited tungsten sulfide film averaged over the 40 nm film thickness and on the surface as measured by ToF-ERDA and XPS, respectively. The film was deposited on silicon at 150 °C using 500 cycles.

Element	Average (at-%)	Surface (at-%)
	ToF-ERDA	XPS
W	37.9±0.2	24.7
S	42.0±0.7	21.8
S/W	1.11±0.02	0.88
C	7.1±0.4	29.5
N	3.3±0.3	1.9
O	3.8±0.3	22.1
H	5.8±1.2	Not detectable

Table II. Elemental surface composition of tungsten sulfide films as-deposited and after annealing as analyzed by XPS. The films were deposited on silicon at 150 °C using 100 cycles and the annealing was done in H₂S/N₂ atmosphere for 1 h.

Element	As-deposited	300 °C	400 °C	500 °C
	(at-%)	(at-%)	(at-%)	(at-%)
W	22.6	21.4	16.2	17.1
S	19.6	26.0	29.5	26.7
S/W	0.87	1.22	1.82	1.56
C	30.2	33.8	37.9	27.9
N	3.1	1.8	1.0	0.8
O	24.6	16.9	14.2	27.5

Table III. Reported WS₂ ALD processes and characteristics of deposited films.

Precursors	Deposition (annealing) temperature (°)	Growth rate (Å/cycle)	Satura tion	Thickness (nm)	Grain size (nm)	S/W ratio	Ref.
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WF ₆ + H ₂ S ^b	300–350	~1	- ^a	10–300	5–100	-	47,49
WF ₆ + H ₂ plasma + H ₂ S	250–450	~0.2	yes	~1–3	~10	1.8±0. 1	43–45
	450	~0.2	yes	<1–5	up to 200	1.8±0. 1	46
WCl ₅ + H ₂ S	390	1.25	- ^a	<5	cryst. ^c	-	53
W(CO) ₆ + H ₂ S	165–205	~0.2	yes	20–40	amorph	2.05	50
	400	3.6	- ^a	175	~5	-	51
W(CO) ₆ + H ₂ S plasma	350	~1	yes	3–20	3–7	1.94	52

^aNot evaluated, ^bno growth unless ZnS substrate or ZnEt₂ pulses were applied, ^cfilm crystalline, but grain size not indicated.

FIG. 1. TGA of $W_2(NMe_2)_6$ (structure shown as an inset) under N_2 atmosphere.

FIG. 2. Growth rate and S/W ratio versus a) $W_2(NMe_2)_6$ and b) H_2S pulse length. c) Film thickness versus number of ALD cycles. d) Growth rate and S/W ratio versus deposition temperature. Film thicknesses were measured by EDS (a,b,d) or XRR (c). S/W ratio was measured by EDS. Unless otherwise noted, the films were deposited on native oxide covered silicon substrates at 150 °C using 500 cycles with 1 s $W_2(NMe_2)_6$ and 2 (a) or 4 s (c,d) H_2S pulses separated by 3 (a,b) or 2 s (c,d) N_2 purges. The line in c) represents a linear fit to the data, whereas the other lines are only to guide the eye.

FIG. 3. a) Raman spectra and b) grazing incidence X-ray diffractograms of tungsten sulfide films as-deposited and after annealing at different temperatures. The films were deposited on silicon at 150 °C using 100 cycles and the annealing was done in H_2S/N_2 atmosphere for 1 h. The Raman and XRD peaks of WS_2 were indexed according to Ref.66 and Powder Diffraction File (PDF) 8-0237, respectively.

FIG. 4. X-ray photoelectron spectra of a) W 4f and b) S 2p regions. The films were deposited on silicon at 150 °C using 100 cycles. The annealing was done in H_2S/N_2 atmosphere for 1 h.

FIG. 5. AFM images and roughness (R_q) values of tungsten sulfide films as-deposited and after annealing at different temperatures. Note the different height scale for the sample annealed at 500 °C. The films were deposited on silicon at 150 °C using 100 cycles and the annealing was done in H_2S/N_2 atmosphere for 1 h.

FIG. 6. a) Thickness of annealed tungsten sulfide films, where the red line represents linear fit to the data and arrow shows the estimated thickness of the 10 cycle film assuming linear growth. b) AFM images of annealed tungsten sulfide films. The films were deposited at 150 °C and annealed at 400 °C for 1 h.

FIG. 7. a) Raman spectra of WS_2 films of different thicknesses after annealing at 400 °C. b) Raman spectrum of a 25 cycle WS_2 film annealed at 400 °C showing the modes fitted between 300 and 450 cm^{-1} . c) Fitted positions of the A_{1g} , E_{2g}^1 , and 2LA(M) modes. d) Frequency difference $A_{1g}-E_{2g}^1$. Open and crossed symbols in c) and d) represent

literature values from Berkdemir et al. (CVD-grown flakes)⁶⁶ and Zhao et al. (exfoliated flakes),⁷⁴ respectively.

FIG. 8. a) Low and b) high magnification HAADF-STEM images of a 50 cycle WS₂ film annealed at 400 °C. c) (002) (dashed) and (100) or (101) planes (solid) highlighted in the high magnification image along with the estimated interplane distances.